TRANSIENT CARBON MONOXIDE CONTROL FOR PEM FUEL CELL SYSTEMS

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Introduction. Hydrocarbon fuels such as gasoline, natural gas, or methanol are being considered as the hydrogen source for PEM fuel cell systems for transportation applications. The partial oxidation and steam reforming processes used to generate hydrogen from these hydrocarbon fuels produce hydrogen-rich gas streams that contain carbon monoxide (CO) and possibly other contaminants at levels that hurt the performance of proton exchange membrane (PEM) fuel cell stacks. A gas clean-up reactor removes the carbon monoxide and contaminants to levels that the PEM fuel cell can tolerate. Transients expected in transportation applications present a design challenge for a gas clean-up reactor, as the flow rates and gas compositions change as the fuel processor generates the hydrogen flow to supply the varying power needs through a drive cycle. Limitations on the transient performance might limit the applicability of hydrocarbon fuel processing to transportation or may require more batteries to handle load peaking.

The Fuel Cell Engineering Team at Los Alamos National Laboratory has been researching methods for controlling carbon monoxide and other contaminants emitted from hydrocarbon fuel processors. Our recent focus has been on the development of gas clean-up reactors and associated controls for transient gasoline fuel processing and to develop computer models of those reactors for analysis and design tools.

Transient gas clean-up experiments have been conducted with a Los Alamos prototype reactor operating on the principle of preferential oxidation (PROX) of carbon monoxide over a catalyst. Our current objective is to demonstrate PROX hardware at an automotive scale (50 kWe equivalent flows) with the capability to control outlet CO concentrations to fuel cell quality through transients that might be encountered in an automotive application. PROX operating experience was acquired in our expanded experimental facility and in collaboration with industrial partners.

50 kWe PROX and Test Facility. A 50 kWe modular PROX test reactor was fabricated. The PROX reactor shown in Figure 1 is a four stage device with an inlet gas conditioning stage and three active catalyst stages. Transient performance is improved and overall volume is reduced by a regenerative design which incorporates heat exchange and air injection and mixing within the length of the catalyst volume. A modular flanged design allows catalysts and catalyst configurations to be changed and the internal geometry to be reconfigured.

The Los Alamos PROX experiment facility was expanded for testing at simulated reformate flows equivalent to a fuel cell operating over the range of 10 kWe to 50 kWe. Hydrogen flow capacity was increased to 140 kWch (based on the LHV) along with the flows of nitrogen, carbon dioxide, and steam to allow simulation of a wet gasoline reformate at these flows. The data acquisition and control system was expanded to provide a transient control capability with the ability to vary timing of control parameters and to simulate transient flows that might come from a reformer. Transient measurement capability was expanded by the addition of on-line gas analyzers for carbon monoxide, methane, and oxygen.

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Experiments were conducted to characterize the steady-state performance of the 50 kWe PROX, to identify the response of the PROX to transients in flow rate and gas composition, and to identify CO control strategies for these transients. The set of experiments reported here were conducted with a synthetic gasoline reformate (36% H_2, 28% N_2, 17% CO_2, 17% H_2O) with varying inlet CO concentrations.

Variables involved in mapping the steady-state performance of the 50 kWe PROX include overall flow rate, inlet CO concentration, and inlet temperature setpoints and oxygen stoichiometries for each of the three stages. As an example of steady-state characterization of the PROX, Figure 2 shows the outlet CO concentration as a function of overall oxygen stoichiometry for all three stages of the PROX operating on 100 kWch gasoline reformate with 8000 ppm CO at the inlet. The second stage outlet CO concentrations were measured with the first stage operating at an oxygen stoichiometry of 1.2. The third stage outlet CO concentrations, ranging from 45 to well below 20 ppm, were measured with the first and second stages operating at an overall oxygen stoichiometry of 1.2 and 1.95, respectively.

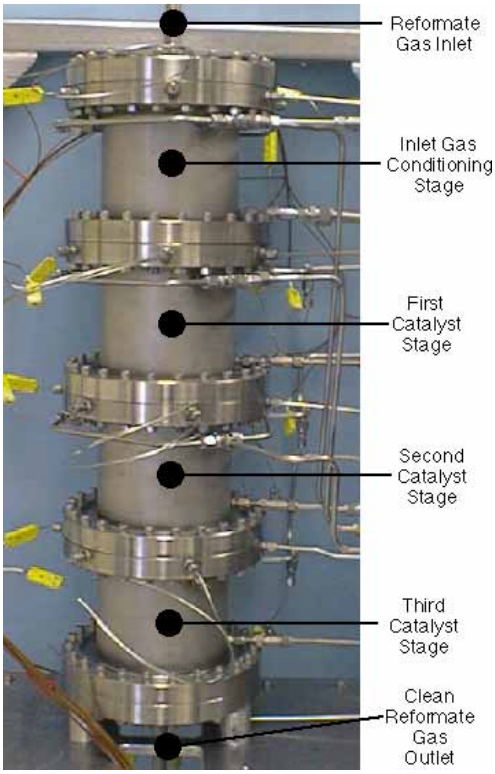

Figure 1. The 50 kWe modular PROX assembled in the Los Alamos test facility. The external plumbing connections shown are the air injection manifolds and the cooling-water inlets and outlets for each stage.

Two types of transient response experiments were conducted with the 50 kWe PROX. The first type was measurement of the outlet CO concentration response to a 90 second pulse increase in the inlet CO concentration from 8000 ppm to 12000 ppm. This response is shown in Figure 3 for two cases: one where the air injection flow rates were held steady through the pulse (no control), and one where the air injection flow rates were held proportional to the inlet CO flow (controlled). With no control, the inlet CO pulse produced an outlet CO pulse rising from approximately 30 ppm CO to above 1500 ppm CO. With control, the outlet CO concentration was held constant through the transient. This experiment illustrates a method of outlet CO control with a transient inlet CO concentration at constant overall flow rate.

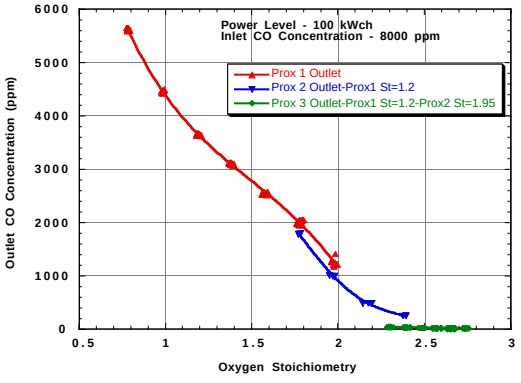

Figure 2. Outlet CO concentrations as a function of overall oxygen stoichiometry are shown for the three stages of the 50 kWe PROX.

The second type of transient response experiment is illustrated in Figure 4. Here, a step increase in the overall flow rate was made from 50 kWch to 100 kWch with the inlet gas composition held constant with an inlet CO concentration of 8000 ppm. This type of transient simulates an increase in power demand from a fuel cell system. The figure illustrates that the timing of the increase in air injection flow rates is critical to control of the outlet CO concentration. A small pulse of 65 ppm CO magnitude

was observed when the air injection flow rates follow the total flow rate increase, while no pulse of CO was observed when the air injection flow rates were increased before the total flow rate increase.

ADL / LANL / Plug Power Fuel Cell Demonstration on Gasoline. A standalone PROX subsystem was developed for use in the demonstration of a gasoline-powered PEM fuel cell system by the team of Arthur D. Little Inc., Plug Power, L.L.C., and Los Alamos National Laboratory. That subsystem was designed and fabricated based on a scaled down version of our 50 kWe PROX concept. Operating points for the air injection and temperature setpoints to obtain outlet CO concentrations below 50 ppm were determined during a limited period of testing at Los Alamos

The PROX subsystem was built into a standalone test stand with a LabVIEW data acquisition and control system at Los Alamos and then shipped to the Cambridge, MA, laboratory of Arthur D. Little, Inc. (now Epyx Corporation) where the PROX subsystem was integrated with the partial oxidation (POX) fuel processor and fuel cell system. Successful system tests were completed with the system operating on both gasoline and ethanol feed streams, with the PROX effluent typically containing less than 50 ppm CO and below 20 ppm CO for significant stretches of the test. Both the Plug Power fuel cell stack and a Ballard Mk.V fuel cell stack were operated on the PROX effluent.

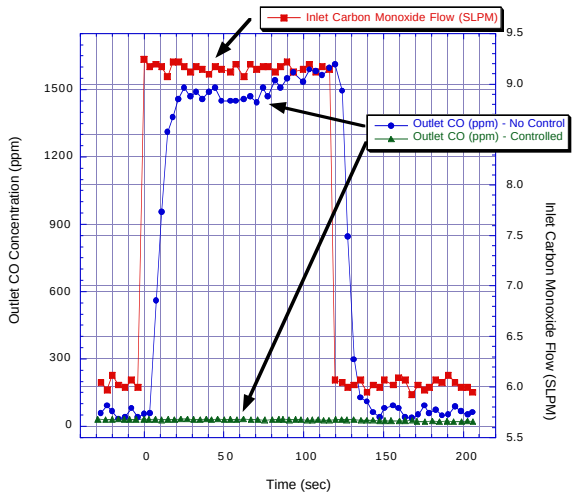

Figure 3. Outlet CO concentrations measured as a function of time for a 90 second pulsed increase in inlet CO concentration from 8000 ppm to 12000 ppm as shown by the inlet carbon monoxide flow. The overall flow rate corresponded to a 50 kWch (based on LHV of hydrogen) synthetic gasoline reformate. Air injection flow rates were held constant for the No Control curve, while air injection flow rates were held proportional to the inlet CO flow for the Controlled curve.

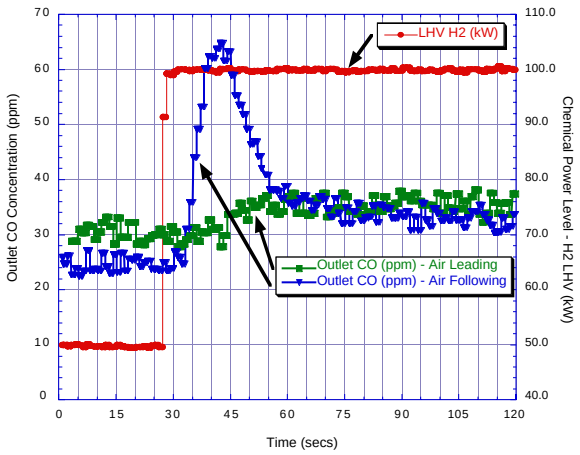

Figure 4. Outlet CO concentrations measured as a function of time for a step increase in overall flow rate from 50 kWch to 100 kWch as shown by the curve labeled LHV H2. The inlet gas composition of synthetic gasoline reformate is held constant with 8000 ppm CO.

Figure 5 shows a time snapshot of the data recorded on the outlet CO concentration of the PROX operating on gasoline reformate from the ADL POX fuel processor. During this time snapshot, the PROX was operated steady-state with fixed air injection and temperature setpoints. Transients

in the outlet CO concentration were measured at regular intervals possibly caused by variations in inlet CO concentration to the PROX, other variations in gas composition, or variations in total flow rate. These observed transients suggested the need for transient PROX control and performance and motivated much of our research and development this year.

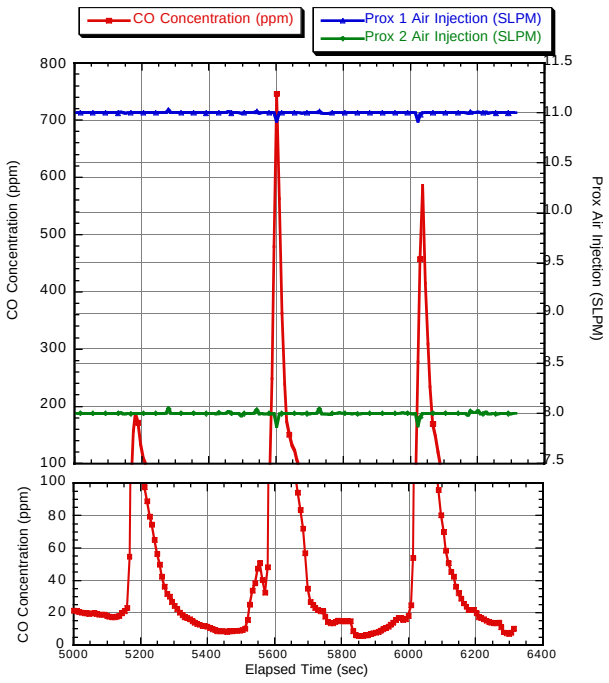

Figure 5. Outlet CO concentration as a function of time from the PROX operating on gasoline reformate from the Arthur D. Little multifuel processor. PROX air injection flow rates were held constant through this time period. The range 0-100 ppm CO is expanded to show the detail of the outlet CO concentration.

PROX Modeling. Development of computer models of PROX operation is a key part of the LANL PROX technology development. We have completed work on a computer model of steady-state operation of our PROX concept, and have used it for sizing of components such as the heat exchangers, investigating scenarios of operation such as variation of flow rates and inlet CO concentration, and for experimental data analysis. Outlet gas composition from each stage is predicted based on a 1-D plug-flow reactor model with an empirical fit to data from our single-stage experiments conducted last year. The model incorporates calculations for the pressure drop through the PROX internal passages and for the gas to liquid coolant heat exchange in the interstage gas coolers. Work is progressing toward the goal of developing models of transient PROX operation with detailed reactor models incorporating chemical kinetics and heat transfer. These models will be used for experimental analysis, design and optimization, and development of control system algorithms.

Future Work. Future work will focus on the development and refinement of PROX technology to meet the requirements for PEM fuel cell systems. The existing 50 kWe PROX and experimental test facility will be used to conduct parameterization and optimization experiments to support development of a transient PROX model. Partial oxidation fuel processors from both Epyx Corp. and Hydrogen Burner Technology will be installed for experiments on fuel system integration and performance, and for comparison of real versus synthetic reformate. We will continue to work with industrial partners such as Energy Partners to integrate and test LANL PROX hardware in their fuel cell systems.

A second focus for future work is the refinement of PROX technology for commercialization. This includes catalyst development and optimization for the automotive environment. A design-for-manufacturing exercise begun this year will continue. LANL will work with industrial partners to develop improved concepts for manufacturing engineering applied to the PROX including sensors, controls, and reactor design.